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(54) Composite metal hydroxide, a method of preparation and its application

(57) A composite metal hydroxide is produced by reacting magnesium-containing aqueous solution (X) including water soluble zinc compound,wherein magnesium ion concentration is 0.01 to 1 mol/liter, with alkaline material (Y) at a specific reaction equivalent ratio. Further, a composite metal hydroxide represented by the following general formula (1) is produced by hydrothermally treating thus obtained composite metal hydroxide within a temperature range of 100 to 200°C for aging in chlorine-containing aqueous solution having a specific chlorine ion concentration.

$$Mg_{1-x}Zn_x(OH)_2 \qquad (1)$$

wherein x indicates a positive number within a range of $0.003 \leqq x \leqq 0.1$.

A uniform metallic solid solution can be obtained as a composite metal hydroxide by the above series of processes. Further, its crystal shape can be controlled thereby so as to restrain occurrence of secondary aggregation. Still further, a flame retardant high-molecular composition, obtained by including thus obtained composite metal hydroxide into a high-molecular composition, exerts high flame retardancy and shows superiority in mechanical strength.

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Description

The present invention relates to a method of producing a composite metal hydroxide of a uniform solid solution, a composite metal hydroxide obtained thereby and its application to produce a flame retardant high-molecular composition superior in flame retardancy and mechanical strength.

A demand for flame retardancy on resin composition or rubber composition has been increased year by year since a critical conflagration occurred in the past.

To respond to such a strong demand for improving flame retardancy, various flame retardants are marketed at present. Among all, in view of safety in manufacturing or using, a demand for improving flame retardancy has severely been increased centered on non-haloganated flame retardants. Under such a situation, metal hydroxides have come to be focused upon.

However, since a dehydration temperature of, for example, aluminium hydroxide is low (about 190°C) among the above metal hydroxides, there is a drawback that the kinds of applicable resins are limited in order to retain a molding temperature below the temperature of dehydration. In the meantime, since an initial dehydration temperature for magnesium hydroxide is about 340°C, there is almost no limitation of the kinds of resins, However, a large amount has to be added to obtain flame retardancy, resulting in deterioration of physical properties inherent in resins. There have been in practice may problems

To solve these problems, for example, a composite metal hydroxide is proposed in Japanese Patent Provisional Publication (Tokkaihei) 6-41441. Compared with a magnesium hydroxide, the composite metal hydroxide realizes flame retardancy using a lower amount. However, when using zinc and magnesium hydroxide for producing a composite metal hydroxide, basic salts and oxides (zinc oxides) may be caused as by-products by characteristics of zinc as a solid solution element in a conventional method. In this way, it is difficult to obtain a composite metal hydroxide of a uniform solid solution and realize the desired properties thereof such as flame retardancy and mechanical strength.

The present invention aims to provide a method of producing a composite metal hydroxide of a uniform solid solution having excellent flame retardancy, a composite metal hydroxide obtained thereby and a flame retardant high-molecular composition superior in mechanical strength.

In a first aspect, the invention provides a method of producing a composite metal hydroxide characterized by reacting magnesium-containing aqueous solution (X) including water soluble zinc compound wherein magnesium ion concentration is 0.01 to 1 mol/liter with alkaline material (Y) at a reaction equivalent ratio (X:Y) of X:Y=1:1.01 to 1:1.20.

A second aspect of the invention is a method of producing a composite metal hydroxide wherein the produced composite metal hydroxide is hydrothermally treated at a temperature within a range of 100 to 200°C in chlorine-containing aqueous medium wherein chlorine ion concentration is 0.5 to 2.0 mol/liter.

A third aspect of the invention is a method of producing a composite metal hydroxide wherein the produced metal hydroxide is heated in the presence of reaction mother liquor at a temperature within a range of 80 to 150 °C and only the crystal surface thereof is substituted for nickel by adding water soluble nickel compound solution

A forth aspect of the invention is a composite metal hydroxide obtained by a method according to the above first or second aspect represented by the following general formula (1);

$$Mg_{1-x}Zn_x(OH)_2 \quad (1)$$

wherein x indicates a positive number within a range of $0.003 \leqq x \leqq 0.1$.

A fifth aspect of the invention is a composite metal hydroxide obtained by a method according to the third aspect represented by the following general formula (2);

$$Mg_{1-x-y}Zn_xNi_y(OH)_2 \quad (2)$$

wherein x indicates a positive number within a range of $0.003 \leqq x \leqq 0.1$ and y indicates a positive number within a range of $0.01 \leqq y \leqq 0.05$.

A sixth aspect of the invention is a flame retardant high-molecular composition containing a composite metal hydroxide represented by the general formula (1) or (2) within a range of 80 to 150 parts by weight based on 100 parts by weight of the high-molecular composition.

It is difficult to stably produce a composite metal hydroxide of a uniform solid solution with Mg in conventional methods, since the stable crystal shape for a hydroxide is not hexagonal. For this reason, the inventors of the present invention have studied reaction processes for obtaining a uniform solid solution. Focused upon two points, the inventors have further accumulated their studies; one is an Mg ion concentration of Zn-containing Mg aqueous solution as a

source of Mg and the other is a reaction equivalent ratio of the Zn-containing Mg aqueous solution and alkaline material. As a result, they reached the conclusion that a composite metal hydroxide of a uniform solid solution represented by the above general formula (1) can be obtained by using Zn-containing Mg aqueous solution wherein Mg ion concentration is set within a range of 0.01 to 1.0 mol/liter and reacting the Zn-containing Mg aqueous solution (X) and alkaline material (Y) at a reaction equivalent ratio of (X:Y)=1:1.01 to 1:1.20. Preferably, they found out that occurrence of secondary aggregation can be restrained because the crystal shape of the composite metal hydroxide can be controlled by hydrothermally treating the composite metal hydroxide obtained by reaction at the above reaction equivalent ratio in an aqueous medium having a specific chlorine ion concentration within a temperature range of 100 to 200°C for aging.

Still preferably the composite metal hydroxide represented by the general formula (2), wherein only the crystal surface is substituted for Ni, can be obtained by heating the obtained composite metal hydroxide within a temperature range of 80 to 150°C in the presence of reaction mother liquor and adding water soluble Ni compound solution therein.

A flame retardant high-molecular composition, wherein the composite metal hydroxide represented by the general formula (1) or (2) is contained within a range of 80 to 150 parts by weight (just abbreviated to parts hereinafter) based on 100 parts of the high-molecular compound, is found to have superior flame retardancy and satisfactory mechanical strength (such as tensile strength) even with less content thereof compared with the conventional ones.

Now, the present invention is described in detail.

The method for producing the composite metal hydroxides of the present invention comprises three versions roughly.

That is, the first step is a reaction for producing the composite metal hydroxide represented by the following general formula (1) by reacting Zn-containing Mg aqueous solution having a specific Mg ion concentration and alkaline material at a specific equivalent ratio. This first reaction is preferable conducted within a temperature range of 10 to 35°C.

$$Mg_{1-x}Zn_x(OH)_2 \quad (1)$$

wherein x represents a positive number within a range of $0.003 \leqq x \leqq 0.1$.

In the general formula (1), x value less than 0.003 is solid solution amount insufficient for emerging the expected effect of the composite metal hydroxide (superior flame retardancy). On the otherhand, x value over 0.1 results in difficulty in forming a uniform solid solution, causing basic salts and oxides as byproduct, since the ionic radius of zinc is larger than that of magnesium. Further, it is difficult to control crystal shape and easy to cause secondary aggregation, which does not bring about the desired effect of the composite metal hydroxide.

As the Zn-containing Mg aqueous solution, such an aqueous solution into which Zn compound has been added, Mg aqueous solution may

As the source of the Mg aqueous solution, diluted be used. bittern, sea water, magnesium nitrate and the like are possibilities, in which Mg ion concentration should be set within a range of 0.01 to 1 mol/liter. Preferably, it is within a range of 0.03 to 0.3 mol/liter. If diluted bittern or sea water is used, Mg ion concentration over 1 mol/liter overwhelmingly causes by-products of basic salts, resulting in difficulty in forming a uniform solid solution. In addition, the Mg ion concentration may be measured by a chelatometric titration method, an ICP emission spectrochemical analysis and the like. Measurement is, however, not critical as long as it is a method for generally analyzing ion concentration in aqueous solution.

As the Zn compound to be added into the Mg aqueous solution, any water soluble zinc compound, such as zinc nitrate or zinc chloride, is included with no limitation. The addition amount thereof based on the Mg aqueous solution is preferably set within a range of 0.3 to 10 mol % based on the Mg in the aqueous solution, more preferably 1 to 7 mol %. An addition amount less than 0.3 mol % is too small an amount of solid solution to give the desired effects of a composite metal hydroxide. On the other hand, that over 10 mol % results in difficulty in forming a uniform solid solution since the zinc ionic radius is larger than that of magnesium, causing basic salts and oxides as by-products. Further, it is difficult to control crystal shape and easy to cause secondary aggregation, which shows a tendency that the desired effects of the composite metal hydroxide cannot be obtained.

Still further, as the alkaline material to be reacted with the Zn-containing Mg aqueous solution having a specific Mg ion concentration, calcium hydroxide, sodium hydroxide and the like are possibilities.

The reaction ratio of the Zn-containing Mg aqueous solution (X) and the alkaline material (Y) needs to be set at the equivalent ratio (X:Y)=1:1.01 to 1:1.20, Preferably, it is set at X:Y=1:1.03 to 1:1.10. When the alkaline material (Y) is less than 1.01 of the reaction equivalent ratio, by-products of basic salts may be identified, preventing formation of a uniform solid solution thereby, while when it is over 1.20, by-products of oxides may be identified, causing difficulty in controlling crystal shape resulting in easiness in occurrence of secondary aggregation.

The preferred combination of the Zn-containing Mg aqueous solution and the alkaline material is sea water (Mg aqueous solution) into which zinc chloride, water soluble zinc compound, is added and calcium hydroxide (limemilk)

as an alkaline material. These are chosen in view of stability of the produced composite metal hydroxide and the manufacturing cost.

An optional second step, following the method of producing the composite metal hydroxide as above is described here.

The second step comprises thermally treating the composite metal hydroxide represented by the general formula (1) produced in the first step in chlorine-containing aqueous medium with a specific chlorine ion concentration within a temperature range of 100 to 200°C, so as to age the composite metal hydroxide.

As the chlorine-containing aqueous medium, aqueous solutions of calcium chloride, sodium chloride, magnesium chloride, potassium chloride and the like may be used. Calcium chloride aqueous solution is preferred as the chlorine-containing aqueous medium in view of controllability of the crystal shape of the composite metal hydroxide. Further, the chlorine ion concentration in the chlorine-containing aqueous medium should be set within a range of 0.5 to 2 mol/liter. Preferably, it is within a range of 0.5 to 1.0 mol/liter. Low concentration of chlorine ion, less than 0.5 mol/liter, may cause insufficient controllability of crystal shape of the composite metal hydroxide, resulting in the easiness in occurrence of secondary aggregation. On the other hand, that over 2 mol/liter may cause basic salts and oxides as by-products, resulting in difficulty in forming a uniform solid solution.

The chlorine ion concentration may be measured by a general method for analyzing ion concentration in solution, such as a chelatometric titration method or an ICP emission spectrochemical analysis.

For the aging conditions for the thermal treatment, the temperature should be set within a range of 100 to 200°C and the pressure should be within a range of 0.5 to 10kg/c m^2 concomitantly.

Thus obtained composite metal hydroxide is represented by the general formula (1). The crystals may further grow and secondary aggregation may decrease through the second step, which results in more preferable flame retardants in view of various properties such as compatibility with a high-molecular compound, dispersibility, appearance of the formed product or mechanical strength.

Next, a third, optional, step following the method of producing the composite metal hydroxide as the second step is described. The composite metal hydroxide obtained by this step is such as represented by the general formula (2), a solid solution comprising three metals of Mg, Zn and Ni.

$$Mg_{1-x-y}Zn_xNi_y(OH)_2 \quad (2)$$

wherein x represents a positive number within a range of $0.003 \leqq x \leqq 0.1$ and y represents a positive number within a range of $0.01 \leqq y \leqq 0.05$.

In the general formula (2), x value less than 0.003 is too small an amount of solid solution to emerge the desired effects (superior flame retardancy) of a composite metal hydroxide. On the other hand, that over 0.1 mol % results in difficulty in forming a uniform solid solution since the ionic diameter of zinc is larger than that of magnesium, causing by-products of basic salts and oxides. In addition, it may cause difficulty in controlling crystal shape and easiness in occurrence of secondary aggregation, which does not bring about the desired effect of composite metal hydroxide. In the meantime, y value less than 0.01 may cause insufficiency of nickel substitution amount on the crystal surface, which does not fully emerge the desired effect of the composite metal hydroxide. In addition, that over 0.05 may cause cost increase and also saturation of the nickel substitution amount on the crystal surface, resulting in by-products of free nickel hydroxide and the like.

In the third step, the composite metal hydroxide represented by the general formula (1), which was produced in the second step, is heated in the presence of reaction mother liquor within a temperature range of 80 to 150°C and water soluble nickel compound solution is added therein so as to substitute only the crystal surface for Ni, resulting in the composite metal hydroxide represented by the general formula (2). Alternatively the third step may be carried out after the first step, omitting the second step.

As the water soluble nickel composite solution, aqueous solutions of nickel chloride, nickel nitrate and the like are possibilities. Among all, it is preferable to use nickel chloride in view of reactivity with composite metal hydroxide. Further, the mixing ratio of such water soluble nickel compound solution is preferably set within 1 to 5 mol % based on the composite metal hydroxide of a reaction mother liquor. Particularly, it is preferable to be within 1 to 3 mol %.

In the meantime, a heating condition in adding water soluble nickel compound solution, as mentioned above, is set within a temperature range of 80 to 150°C. Particularly, it is preferable to set within a temperature range of 90 to 120°C. By setting as such, it becomes possible to substitute effectively only the crystal surface for nickel. A lower temperature may cause free nickel hydroxides as by-products due to insufficient substitution. On the other hand, a higher temperature may cause excessive nickel substitution extending into the inside of crystal structure. In both ways, the desired effect is not realized.

For the composite metal hydroxide represented by the general formula (1) obtained through the first or second

step, or represented by the general formula (2) obtained through the third step, the crystal size is 0.2 to 4 μm, more preferably 0.2 to 2 μm, most preferably 0.5 to 1.5 μm, and that with almost no or less secondary aggregation. This means that the average secondary particle size is 0.2 to 4 μm, more preferably 0.2 to 2 μm, most preferably 0.5 to 1.5 μm, and also the BET specific surface area is 1 to 20 m^2/g, preferably 3 to 15 m^2/g, most preferably 6 to 12 m^2/g.

Since each value for the composite metal hydroxide is set within a range as above, it becomes possible to retain superior effects in compatibility with high-molecular compounds such as resin or rubber, dispersibility, forming capability, appearance of the formed products, mechanical strength and the like to be mentioned below. The above average secondary particle diameter is a value measured by the microtrack method on sample powder, which was dispersed by a ultrasonic treatment, in 0.2% sodium hexametaphosphate aqueous solution.

The BET specific surface area is a value in accordance with an N_2 adsorption method.

Thus obtained composite metal hydroxide represented by the above general formula (1) or (2), may be used as a flame retardant as it is However, it may be possible to additionally conduct surface treatment with finishing agents such as various fatty acids, phosphoric acid ester, coupling agents and the like. The various finishing agents may be used solely or in combination of two or more.

As the various fatty acids, higher fatty acids having 10 or more carbon atoms such as stearic acid, oleic acid, erucic acid, palmitic acid, lauric acid and behenic acid, and alkali metal salts thereof may be listed. In addition, as the phosphate esters, mono- or diesters of orthophosphoric acid with oleyl alcohol or stearyl alcohol, mixtures of these, acid type or alkali metal salts or amine salts thereof may be listed.

As the above coupling agents, silane-coupling agents such as vinylethoxysilane, vinyl-tris(2-methoxy-ethoxy)silane, γ-methacryloxypropyltrimethoxysilane; γ-glycidioxypropyltrimethoxysilane, γ-aminopropyltrimethoxysilane, β-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, γ-mercaptopropyltrimethoxysilane, titanate coupling agents such as isopropyltriisostearoyl titanate, isopropyltris(dioctylpyrophosphate)titanate, isopropyltri(N-aminoethyl-aminoethyl) titanate and isopropyltridecylbenzenesulfonyl titanate; aluminium coupling agents such as acetoalkoxyalminium diisopropylate.

As the above surface treatment with various finishing agents, a conventional moisture or dry method is available, with no limitation.

Then, by adding the composite metal hydroxide represented by the general formula (1) or (2) as a flame retardant into the high-molecular compound, a flame retardant having high-molecular composition can be obtained.

As the above high-molecular compound, general resin, rubber and the like may be used . For example, a copolymer of polyethylene or ethylene with other α-olefin, a copolymer of ethylene with vinyl acetate, ethyl acrylate or methyl acrylate, polypropylene, a copolymer of propylene with other α-olefin, polybutene-1, polystyrene, a styrene-acrylonitrile copolymer, thermoplastic resin such as vinyl acetate, polyacrylate, polymerhacrylate, polyurethane, polyester, polyether, polyamide, themosetting resins such as phenolic resin, melamine resin, epoxy resin, unsaturated polyester resin, alkyd resin, ethylene-propylene-diene rubber, stylene-butadine rubber, acrylonitrile-butadiene rubber, butyl rubber, isoprene rubber, chlorosulfonated polyethlene and the like. These high-molecular compounds are appropriately selected.

At that time, the mixing ratio of the composite metal hydroxide represented by the general formula (1) or (2) is selected appropriately depending on the kinds of the above high-molecular compounds and the like. It is set within a range of 80 to 150 parts by weight based on 100 parts of the high-molecular compound. Particularly, it is preferably 100 to 130 parts.

A mixing ratio less than 80 parts may cause insufficient flame retardancy, while that over 150 parts may cause deterioration in mechanical strength such as tensile strength. Further, the composite metal hydroxide represented by the general formula (1) or (2) may be used solely or in combination as long as its mixing ratio is set within the above range.

Further, various additives may be added appropriately other than the above composite metal hydroxide represented by the general formula (1) or (2) into the flame retardant high-molecular composition of the present invention. For example, a general flame retardant aid such as carbon fine powder, red phosphorus is a possibilty. Moreover, lubricants, antioxidants, ultraviolet inhibitors, antistatic agents, pigments, foaming agents, plasticizers, fillers, reinforcing materials, crosslinking agents and the like may be used.

The flame retardant high-molecular compound can be obtained by adding the composite metal hydroxide represented by the general formula (1) or (2) into the high-molecular compound at a specific ratio, mixing and then kneading thereof. As a method for mixing and kneading thereof, conventional methods such as single-screw or twin-screw extruder, a roll, a Banbury mixer and the like may be used, with no limitation.

Then, as a method for forming with thus obtained flame retardant high-molecular compound, a suitable molding method is selected appropriately depending on the kinds of the high-molecular compounds, the kinds of desired molded products and the like with no limitation. For example, injection molding, extrusion, blow molding, press molding, rotational molding, calendering, sheet forming, transfer molding, laminate molding, vacuum molding and the like may be used.

Now, the present invention will further be described based on examples with reference to comparative examples.

EXAMPLE 1

By dissolving zinc chloride, a reagent of the first grade, into ionic bittern and diluting thereof with deionized water, 300-liter mixture aqueous solution with 0.14 mol/liter Mg ion concentration and 0.008 mol/liter Zn ion concentration was produced. In the meantime, as the alkaline material, 51-liter limemilk with 0.9 mol/liter was produced. Both of them were mixed in such a manner that the reaction equivalent ratio is mixture aqueous solution:limemilk=1:1.03 by charging thereof consecutively with stirring into a continuous reaction vessel of 50-liter effective volume. Then, this reactant was emulsified into calcium chloride aqueous solution with 1.0 mol/liter chlorine ion concentration, and thermally treated at 150°C for two hours by putting thereof into an autoclave of 100-liter effective volume with a stirrer . Thereafter, it was filtrated by a filter press, washed with water, dehydrated, dried in an oven and then pulverized, thus producing the composite metal hydroxide as an objective.

EXAMPLE 2

Emulsification of the reactant in example 1 was conducted in sodium chloride aqueous solution with 0.5 mol/liter chlorine ion concentration and the thermal treatment was conducted at 170°C for two hours. Except for that, example 2 was the same as example 1, thus producing the composite metal hydroxide as an objective.

EXAMPLE 3

By dissolving zinc nitrate, a reagent of the first grade, into ionic bittern and diluting thereof with deionized water, 50-liter mixture aqueous solution with 1.0 mol/liter Mg ion concentration and 0.003 mol/liter Zn ion concentration was produced. In the meantime, as the alkaline material, 52-liter limemilk with 1.0 mol/liter was produced. Both of them were mixed in such a manner that the reaction equivalent ratio is mixture aqueous solution:limemilk=1:1.04 by charging thereof consecutively with stirring into a continuous reaction vessel of 10-liter effective volume. Then, this reactant was emulsified into sodium chloride aqueous solution with 2.0 mol/liter chlorine ion concentration, and thermally treated at 150°C for two hours by putting thereof into an autoclave of 100-liter effective volume with a stirrer. Thereafter, it was filtrated by a filter press, washed with water, dehydrated, dried in an oven and then pulverized, thus producing the composite metal hydroxide as an objective.

EXAMPLE 4

The reaction equivalent ratio of the mixture aqueous solution and limemilk of example 3 was changed in such a manner that mixture aqueous solution:limemilk=1:1.20. Except for that, example 4 was the same as example 3, thus producing the composite metal hydroxide as an objective.

EXAMPLE 5

By dissolving magnesium nitrate and zinc nitrate, reagents of the first grade, into deionized water, 1-liter mixture aqueous solution with 0.9 mol/liter Mg ion concentration and 0.1 mol/liter Zn ion concentration was produced. In the meantime, as the alkaline material, 1-liter sodium hydroxide aqueous solution with 2.04 mol/liter was produced. Both of them were mixed in such a manner that the reaction equivalent ratio is mixture aqueous solution :sodium hydroxide = 1:1.02 by dropping the mixture aqueous solution into sodium hydroxide aqueous solution with stirring, thus producing reactant. This reactant was emulsified into sodium chloride aqueous solution with 1.0 mol/liter chlorine ion concentration, and thermally treated at 150°C for two hours by putting thereof into an autoclave of 3-liter effective volume with a stirrer and thereafter, filtrated by a vacuum filter, washed with water, dehydrated, dried in an oven and then pulverized, thus obtaining the composite metal hydroxide as an objective.

EXAMPLE 6

Synthetic sea water was produced by adding zinc nitrate into 1530-liter decarboxylated sea water (Mg ion concentration: 0.032 mol/liter) in such a manner that Zn ion concentration was 0.002 mol/liter. In the meantime, as the alkaline material, 51-liter limemilk with 1.07 mol/liter alkali ion concentration was produced. Then, both of them were mixed in such a manner that the reaction equivalent ratio is synthetic sea water:limemilk=1:1.05 by charging thereof consecutively with stirring into a continuous reaction vessel of 250-liter effective volume. Then, this reactant was emulsified into calcium chloride aqueous solution with 1.2 mol/liter chlorine ion concentration, and thermally treated at 150°C for two hours by putting thereof into an autoclave of 100-liter effective volume with a stirrer. Thereafter, it was filtrated by a filter press, washed with water, dehydrated, dried in an oven and then pulverized, thus producing the composite

metal hydroxide as an objective.

EXAMPLE 7

The reaction mother liquor after being thermally treated at 150°C for two hours in example 6 was cooled down to 100°C. And 3.5-liter nickel chloride aqueous solution with 0.3 mol/liter Ni ion concentration was added therein with stirring for aging with heating at 100°C for 30 minutes. Except for that, example 7 is the same as example 6.

EXAMPLE 8

The ratio of nickel chloride aqueous solution based on the produced composite metal hydroxide was changed to 1mol %. Except for that, example 8 was the same as example 7.

EXAMPLE 9

The ratio of nickel chloride aqueous solution based on the produced composite metal hydroxide was changed to 5 mol % and the aging condition with heating was changed to 150°C for 30 minutes. Except for that, example 9 was the same as example 7.

EXAMPLE 10

The reaction mother liquor after being thermally treated at 150°C for two hours in example 3 was cooled down to 100°C. And 3.9-liter nickel chloride aqueous solution with 0.4 mol/liter Ni ion concentration was added therein with stirring for aging with heating at 100°C for 30 minutes. Except for that, example 10 is the same as example 6.

COMPARATIVE EXAMPLE 1

By dissolving zinc chloride, a reagent of the first grade, into bittern, 30-liter mixture aqueous solution with 1.7 mol/liter Mg ion concentration and 0.085 mol/liter Zn ion concentration was produced. In the meantime, as the alkaline material, 46-liter limemilk with 1.0 mol/liter alkaline ion concentration was produced. Then, both of them were charged into a continuous reaction vessel of 2.5-liter effective volume with stirring for reaction in such a manner that mixture aqueous solution:limemilk =1:0.9 at a reaction equivalent ratio. Further, this reactant was put into an autoclave of 100-liter effective volume with a stirrer for thermal treatment at 150°C for two hours. Thereafter, it was filtrated by a filter press, washed with water, dehydrated, dried in an oven and then pulverized, thus producing the composite metal hydroxide as an objective.

COMPARATIVE EXAMPLE 2

The reaction equivalent ratio of the mixture aqueous solution and the limemilk was changed to 1:1.05. Except for that, comparative example 2 was the same as comparative example 1 so as to obtain the resultant product.

COMPARATIVE EXAMPLE 3

The reaction equivalent ratio of the mixture aqueous solution and the sodium hydroxide of example 5 was changed to 1:1.25. Except for that, comparative example 3 was the same as example 5 so as to produce the resultant product.

COMPARATIVE EXAMPLE 4

The reaction equivalent ratio of the mixture aqueous solution and the sodium hydroxide of example 5 was changed to 1:1.00. Except for that, comparative example 4 was the same as example 5 so as to produce the resultant product.

COMPARATIVE EXAMPLE 5

A mixture aqueous solution of 1.1 mol/liter Mg ion concentration and 0.055 mol/liter Zn ion concentration was produced. In the meantime, the reaction equivalent ratio of the mixture aqueous solution and the limemilk was set at 1:1.05. Except for that, comparative example 5 was the same as comparative example 1.

COMPARATIVE EXAMPLE 6

The mixture aqueous solution of example 1 was changed to that of 0.14 mol/liter Mg ion concentration and 0.019 mol/liter Zn ion concentration. Except for that, comparative example 6 was the same as example 1.

COMPARATIVE EXAMPLE 7

The mixture aqueous solution of example 1 was changed to that of 0.88 mol/liter Mg ion concentration and 0.12 mol/liter Zn ion concentration. Except for that, comparative example 7 was the same as example 1.

Each of chemical composition, average secondary particle diameter and BET specific surface area of thus obtained various composite metal hydroxides was measured. The results are shown in the following tables 1 and 2.

The chemical composition was quantitatively determined by an x-ray fluorescence analysis, and a chelatometric titration method, an ICP emission sepctrochemical analysis or the like on the mixture wherein a composite metal hydroxide was dissolved in hydrochloric acid for quantification of content by element, and also identified and measured on lattice constant by x-ray diffraction to judge whether a uniform solid solution was realized or not.

The above average secondary particle size was measured by a microtrack method after conducting ultrasonic dispersion treatment on sample powder in 0.2% sodium hexametaphosphate aqueous solution.

The BET specific surface area was measured by an N_2 adsorption method.

TABLE 1

CHEMICAL COMPOSITION

EXAMPLES	
1	$Mg_{0.95}Zn_{0.05}(OH)_2$
2	$Mg_{0.95}Zn_{0.05}(OH)_2$
3	$Mg_{0.997}Zn_{0.003}(OH)_2$
4	$Mg_{0.997}Zn_{0.003}(OH)_2$
5	$Mg_{0.9}Zn_{0.1}(OH)_2$
6	$Mg_{0.94}Zn_{0.06}(OH)_2$
7	$Mg_{0.92}Zn_{0.06}Ni_{0.02}(OH)_2$

8	$Mg_{0.93}Zn_{0.06}Ni_{0.01}(OH)_2$
9	$Mg_{0.89}Zn_{0.06}Ni_{0.05}(OH)_2$
10	$Mg_{0.967}Zn_{0.003}Ni_{0.03}(OH)_2$

COMPARATIVE EXAMPLES

1	$Mg(OH)_2$+Zn(OH)Cl
2	$Mg(OH)_2$+Zn(OH)Cl
3	$Mg(OH)_2$+ZnO
4	$Mg(OH)_2$+Zn(OH)Cl
5	$Mg(OH)_2$+Zn(OH)Cl
6	$Mg(OH)_2$+Zn(OH)Cl
7	$Mg(OH)_2$+ZnO

TABLE 2

	AVERAGE SECONDARY PARTICLE DIAMETER (μ m)	BET SPECIFIC SURFACE AREA (m^2/g)
EXAMPLES		
1	0.72	10.9
2	0.75	7.9
3	0.86	6.0
4	0.71	9.8
5	0.66	11.9
6	0.83	7.0
7	0.80	7.6
8	0.80	7.6
9	0.79	6.9

10	0.85	6.6
COMPARATIVE EXAMPLES		
1	0.74	8.6
2	0.74	8.9
3	0.61	15.5
4	0.81	6.9
5	0.72	7.8
6	0.78	7.3
7	0.57	16.5

From the above tables 1 and 2, it is found out that a uniform solid solution was obtained in every example.

EXAMPLES 11 TO 15

Next, each composite metal hydroxide (of examples) shown in the following table 3 was suspended into water respectively, heated up to 70°C with stirring. Subsequently, sodium oleate dissolved in advance was added into the composite metal hydroxide by 2 weight % as oleic acid so as to be surface treated. Then, it was dehydrated, washed with water and dried in an oven. Further, as a specimen, 0.2 parts antioxidant and each composite metal hydroxide (of examples), surface treated at ratios shown in the following table 3, were added based on 100 parts ethylene-ethylacrylate copolymer (ethylene acrylate content: 15 weight %, Nippon Petrochemicals Co., Ltd.) so as to be mixed in a blender. After being mixed, it was kneaded by an open-roll mixer at 130°C and further press-molded at 160°C so as to be made into a sheet in 1mm thickness and a sheet in about 3.2mm thickness (1/8 inch) respectively. Then, each of the sheets was punched into a dumbbell-shape and a strip-shape as samples respectively. These samples were subjected to a tensile test in accordance with JIS C3005 and a combustibility test in accordance with UL94VE.

TABLE 3

(parts)

	EXAMPLES				
	11	12	13	14	15
COMPOSITE METAL HYDROXIDE					
EXAMPLE 3	130	--	--	--	--
EXAMPLE 5	--	120	--	--	--
EXAMPLE 7	--	--	110	--	--
EXAPMLE 9	--	--	--	100	--
EXAMPLE 10	--	--	--	---	120

COMPARATIVE EXAMPLES 8 TO 11

Each reaction product (of comparative examples) and $Mg(OH)_2$ shown in the following table 4 were mixed at ratios specified therein. Except for that, each sheet was formed in the same way as that of examples 12 to 19. Then, each sheet was punched into a dumbbell-shape and a stripe-shape as specimens. These specimens were subjected to a

tensile test in accordance with JIS C3005 and a combustibility test in accordance with UL94VE.

TABLE 4

(parts)

	COMPARATIVE EXAMPLES			
	8	9	10	11
COMPOSITE METAL HYDROXIDE				
COMPARATIVE EXAMPLE 1	140	--	--	--
COMPARATIVE EXAMPLE 7	--	140	--	--
$MG(OH)_2$	--	--	140	150

The results of tensile strength and combustibility tests by using these specimens are shown in the following tables 5 and 6.

TABLE 5

	EXAMPLES				
	11	12	13	14	15
FLAME RESISTANCE TEST					
UL94VE (1/8inch thickness)	V-0	V-0	V-0	V-0	V-0
TENSILE STRENGTH					
(kgf/mm^2)	0.97	1.03	1.15	1.21	1.13

TABLE 6

	COMPARATIVE EXAMPLES			
	8	9	10	11
FLAME RESISTANCE TEST				
UL94VE (1/8inch thickness)	B	B	B	V-0
TENSILE STRENGTH				
(kgf/mm^2)	0.89	0.78	0.89	0.79

From the above tables 5 and 6, it is found out that all comparative examples were low in tensile strength and inferior in mechanical strength. Further, good results were not obtained for flame retardancy on comparative examples 8 to 10. On the other hand, good results were obtained for flame retardancy on all examples although composite metal hydroxides were added in lower amounts than in the comparative examples. Still further, tensile strength of examples was superior to that of all comparative examples, which shows that all examples retain high flame retardancy as well as mechanical strength.

EFFECTS OF THE INVENTION

As the above, the composite metal hydroxide represented by the general formula (1) is produced by reacting Zn-containing Mg aqueous solution having a specific Mg ion concentration and alkaline material at a specific reaction equivalent ratio. For this reason, a composite metal hydroxide, a uniform solid solution, wherein Zn is solid solved into Mg system, which is difficult to produce in the conventional methods can be obtained. Preferably, the composite metal hydroxide obtained at this reaction equivalent ratio is aged in aqueous medium having a specific chlorine ion concentration at a specific temperature so as to produce the composite metal hydroxide represented by the general formula (1), whose crystal shape can be controlled, which prevents occurrence of secondary aggregation.

In addition, the composite metal hydroxide represented by the general formula (2) wherein only the crystal surface is substituted for Ni can be obtained by adding water soluble Ni compound solution into the composite metal hydroxide represented by the general formula (1) at a specific temperature in the presence of reaction mother liquor. Thus obtained composite metal hydroxide is a uniform solid solution wherein Zn is solid solved into Mg system. Therefore, the flame retardant high-molecular composition obtained by mixing the composite metal hydroxide represented by the general formula (1) or (2) at a specific volume based on the high-molecular compound exerts high flame retardancy, using lower amounts compared with the conventional ones and shows superiority in mechanical strength.

Claims

1. A method of producing a composite metal hydroxide characterized by reacting magnesium-containing aqueous solution (X) including water soluble zinc compound wherein magnesium ion concentration is 0.01 to 1 mol/liter with alkaline material (Y) at a reaction equivalent ratio (X:Y) of X:Y=1:1.01 to 1:1.20.

2. A method of producing a composite metal hydroxide according to claim 1 wherein the produced composite metal hydroxide is hydrothermally treated at a temperature within a range of 100 to 200°C in chlorine-containing aqueous medium wherein chlorine ion concentration is 0.5 to 2.0 mol/liter.

3. A method of producing a composite metal hydroxide according to claim 2 wherein the produced metal hydroxide is heated in the presence of reaction mother liquor at a temperature within a range of 80 to 150 °C, and only the crystal surface thereof is substituted for nickel by adding water soluble nickel compound solution.

4. A composite metal hydroxide obtained by a method according to claim 1 or 2 represented by the following general formula (1);

$$Mg_{1-x}Zn_x(OH)_2 \quad (1)$$

wherein x indicates a positive number within a range of $0.003 \leqq x \leqq 0.1$.

5. A composite metal hydroxide obtained by a method according to claim 3 represented by the following general formula (2);

$$Mg_{1-x-y}Zn_xNi_y(OH)_2 \quad (2)$$

wherein x indicates a positive number within a range of $0.003 \leqq x \leqq 0.1$
and y indicates a positive number within a range of $0.01 \leqq y \leqq 0.05$.

6. A flame retardant high-molecular composition containing composite metal hydroxide according to claim 4 or 5 within a range of 80 to 150 parts by weight based on 100 parts by weight of the high-molecular composition.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 5727

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DATABASE WPI Section Ch, Week 9531 Derwent Publications Ltd., London, GB; Class A60, AN 95-237040 XP002017451 & JP-A-07 144 919 (KAISUI K.K. ET AL) , 6 June 1995 * abstract *	1	C01F5/00
A D	EP-A-0 498 566 (KAISUI KAGAKU KENKYUJO KK) 12 August 1992 * page 5, line 18 - line 39 * & JP-A-06 041 441	1	
A	EP-A-0 544 502 (KAISUI KAGAKU KENKYUJO KK) 2 June 1993 * page 4, line 46 - line 51 *	1	
A	EP-A-0 517 448 (KAISUI KAGAKU KENKYUJO KK) 9 December 1992 * claim 4 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP-A-0 544 503 (KYOWA CHEM IND CO LTD) 2 June 1993 * claim 5 *	1	C01F C01G C01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	7 November 1996	Clement, J-P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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